Lockheed Martin Space Operations
Science, Engineering, Analysis, and Test
2400 NASA Road 1, P.O. Box 58561 Houston TX 77258-8561
Telephone (281) 333-5411

LOCKHEED MARTIN

September 26, 2000
Subtask Order: 0HECECAYW
Contract: NAS9 -19100
MSAD-00-0521

TO: Sharon LaFuse/EC2

CC: Distribution

VIA: K. E. Lange *Original Initialed by KEL*
F. F. Jeng *Original Initialed by FFJ*
J. F. Keener *Original Initialed by JFK*
J. L. Cox *Original Initialed JLC*

FROM: H. Y. Yeh *Original Signed Jannivine Yeh*

SUBJECT: Analysis Support of the Bioregenerative Water Recovery System (BWRS) Integration Test - Modeling and Data Analysis of the TOC Removal Process and Nitrification Process

Attached please find a copy of the report in support of the Analysis Support for the BWRS Integration Test.

If you have any questions or comments, please call me at 281/333-7682 or email me at jannivine.yeh@lmco.com.

DISTRIBUTION

C. H. Lin	NASA/EC2
Sharon LaFuse	NASA/EC2
M. K. Ewert	NASA/EC2
K. D. Pickering	NASA/EC3
B.W. Finger	Honeywell/EC3
Mellisa Campbell	Hamilton Standard/EC3
Jayesh Gandhi	GB Tech/EC3
Leticia Vega	GB Tech/EC3
Chris Carrier	GB Tech/EC3
Pete Bonasso	GB Tech/EC3
J.C.Almlie	LMSO/EC3
J. L. Cox	C70
B. Duffield	C70
Tony Hanford	C70
F. F. Jeng	C70
J. F. Keener	C70
K. E. Lange	C70
Gina Pariani	LMSO/EC3
Olivia Schultz	LMSO/EC3
Chuck Verostko	LMSO/EC3
Larry Wallace	LMSO/EC3
H. Y. Yeh	C70
Task Order File (2)	

ACRONYMS AND DEFINITIONS

BWRS: Bioregenerative Water Recovery System
BWP: Bioregenerative Water Process
HRT: Hydraulic Residence Time
JSC: Johnson Space Center
MOE: Name of the experimental unit for TOC removal
NH_4^+: Ammonium ions
Nitrates-N: Nitrogen content of the nitrates
N_2: Nitrogen
O_2: Oxygen
SHEMP: Name of the experimental unit mainly for nitrification
TOC: Total Organics Carbon
VSS: Volatile Suspended Solids
WRS: Water Recovery System

OBJECTIVE

The objective of the modeling and analysis support for the WRS Integration Task is to develop the kinetics of the Total Organics Carbon (TOC) Removal process and the Nitrification process based on the data collected from the public domain, to validate the kinetics with the JSC Bioregenerative Water Recovery System (BWRS) experimental data, and to modify the existing WRS ASPEN Plus model's TOC Removal and Nitrification modules by taking into account the kinetics developed from the experimental data. The upgraded model will allow user to conduct WRS bioreactors' performance prediction at various operating conditions.

UPGRADE OF THE BIOREACTOR MODULES OF THE WRS ASPEN PLUS MODEL

1. TOC REMOVAL PROCESS

Literature search and data review

A literature search was conducted to obtain experimental data similar to the operating conditions of the bioreactors for the JSC BWRS, and the data was subsequently used in the development of the reaction kinetics of the TOC Removal process.

Most of the test data available from the public domain are for denitrification with low molecular weight organic carbons as the carbon source for the microorganisms (Ref. 1-8). Limited information is available for TOC removal with nitrate as N_2 and O_2 sources for the microorganisms (Ref. 9-14).

Implementation of the Monod Kinetics to the TOC Module of the WRS ASPEN PLUS Model

Environmental factors, such as temperature, pH, nitrates concentration and carbon concentration can have a significant effect on the reaction rates of the TOC removal/denitrification process. Halling-Sorensen, et al (Ref. 1) proposed that using the Monod Kinetic approach, a combined kinetic equation relating the denitrification process with the influence of carbon concentration to the organism growth rate, can be expressed by the following relationship:

$$dS_{denit}/dt = - u_{max,D}/Y_D * S_{denit}/(K_D + S_{denit}) * S_{TOC}/(K_{TOC} + S_{TOC}) * X_D \quad \text{.........(1)}$$

Assuming that the TOC removal rate equals the denitrifying rate, i.e.

$$dS_{denit}/dt = K * dS_{TOC}/dt \quad \text{.........(2)}$$

Where K = Stoichiometric coefficient

We further assume that the temperature and pH of the system are controlled at constant levels and nitrates are in excess, i.e. the nitrate concentration is not the rate-limiting factor, combining equations (1) and (2) leads to equation (3):

$$dS_{TOC}/dt = - u_{max,D}/Y_D * S_{TOC}/(K_{TOC} + S_{TOC}) * X_D \quad \text{.........(3)}$$

where $u_{max,D}$ = Maximum growth rate of the denitrifying bacteria, day^{-1}

X_D = Biomass concentration of the denitrifying bacteria, mg/l
Y_D = Denitrifying yield coefficient, mg denitrifying bacteria grown (VSS) per mg nitrates-N removed.
S_{denit} = Concentration of substrate to be denitrified, mg/l as nitrate-N
S_{TOC} = TOC concentration in the TOC removal/denitrifying reactor, mg/l
K_D = Saturation constant, mg/l as nitrates-N
t = Residence time, days
K_{TOC} = Saturation constant, mg/l as TOC

Integration of equation (3) leads to equation (4):

$$K_{TOC}*\ln (S_{TOC} / S_{TOC,0}) - (S_{TOC} - S_{TOC,0}) = -K_{RATE}* t \quad\ldots\ldots\ldots\ldots(4)$$

Where $K_{RATE} = u_{max,D}/Y_D*X_D$

A Fortran subroutine using equation (4) for the TOC removal process was implemented into the TOC removal module of the WRS ASPEN Plus model. Testing and verification of the modified model were completed.

Implementation of the Half-Order Reaction Kinetics to the TOC Removal Module of the ASPEN PLUS WRS Model

Harremoes (Ref. 2) proposed that the reaction kinetics for biofilm reactors follow zero-order or half-order reaction kinetics. The reaction follows the zero order reaction kinetics if the substrate fully penetrates the biofilm, otherwise it follows the half-order reaction kinetics when the substrate partially penetrates the biofilm. Some reports (Ref. 11, 14) found that both half-order and zero order reaction kinetics exist in the TOC reduction/denitrification processes under various substrate concentrations.

In the BWRS application, it is assumed that excess nitrates are added to the TOC reduction reactor, making nitrates non-rate limiting. The only rate-limiting factor is, therefore, the TOC concentration. The reaction can be of zero or half-order kinetics, depending on the total organic carbon concentration of the system.

As the basis of this task, half-order reaction kinetics of the TOC removal process was assumed and experimental data were correlated. A FORTRAN block using the half-order kinetics correlation was built into the TOC removal module of the WRS ASPEN PLUS Model. Testing and result verification were completed.

In the near future, as more-experienced-based kinetics are developed, the FORTRAN block can be easily modified for more accurate prediction of the TOC removal reactor's performance.

Validation of the Modified TOC Removal Module

In order to validate the modified TOC removal module, experimental data from the MOE unit were obtained from Karen Pickering/EC3, Barry Finger/Honeywell, and Jayesh Gandhi/GB Tech.

Subsequently, data reduction and correlation were conducted and completed. Results are shown in the following.

Summaries of test data from data reduction and data conversion are tabulated in Tables 1 and 2. Figure 1 shows the relationship between the overall TOC conversion and Hydraulic Residence Time (HRT) for the MOE experimental unit. The relationship between the single-pass TOC conversion and residence time is presented in Figure 2.

In Figure 1, test data collected between 6/22/99 and 4/23/2000 indicate that the TOC conversion and the hydraulic residence time are independent of each other. Figure 2 shows the similar trend for the one-pass TOC conversion and the residence time for the same time frame.

The MOE data collected between 6/22/1999 and 4/23/2000 also indicate that increasing the HRT does not result in higher TOC removal.

As a result of this new finding and to confirm the kinetics, further literature search was conducted to obtain published data in the public domain. Experimental data found in Mendonca's work (Ref. 3) show that the denitrification conversion is independent of hydraulic residence time. These data show that an increase in hydraulic loading or volumetric flow resulted in a long-term increase in the half-order denitrification rate constant. The MOE data collected before 4/23/2000 exhibits the same phenomena as depicted in Figure 3. The nearly constant conversion with increasing hydraulic residence time is due to the higher growth rate of biomass at higher hydraulic loading and shorter hydraulic residence time.

Reference 3, therefore, has confirmed the phenomenon found in the MOE experimental unit for data collected between 6/22/99 through 4/23/2000.

In Table 1 and Figure 1, test data collected between 4/24/2000 and 9/14/2000 show that decreasing the HRT below 6.05 hours would decrease the overall TOC conversion. This suggests that a minimum HRT is required to achieve the optimum conversion of the TOC removal process.

Optimization of the TOC Removal Process

From Table 1 and Figure 1, three data points that are worthwhile for further investigation are HRTs at 6.05, 8.45, and 24.2 hours. Repeating the experiment at these data points will allow us to confirm the optimum hydraulic residence time and to make better judgment on the optimum HRT selection in the near future.

If the downstream nitrification process of the BWP can be improved to a higher processing rate, the lower HRT of the TOC removal process can be selected. This will lead to a higher overall BWP processing rate or the size reduction of the TOC reactor.

Table 1. Summary of Test Data from the MOE Experimental Unit

Test point	Date	Qf, ml/min	Qr, ml/min	HRT, hour	Feed TOC, mg/l	Reactor Inlet TOC, mg/l	Reactor Effl. TOC, mg/l	Overall Conv., %
1	6/22/99	0.4	7.9	105.88	387.64	96.53	81.79	78.90
2	7/19/99	0.79	15.7	53.61	394.10	101.57	86.85	77.96
3	8/10/99	0.87	17.5	48.68	501.57	123.81	105.03	79.06
4	9/7/99	1.05	20.9	40.33	369.28	106.54	93.34	74.72
5	9/26/99	1.22	24.4	34.71	373.56	90.13	75.96	79.67
6	10/5/99	1.48	29.6	28.61	322.83	82.83	70.83	78.06
7	10/11/99	1.75	41.9	24.20	463.60	102.81	87.74	81.07
8	11/12/99	2.53	51	16.74	443.23	116.02	99.79	77.49
9	11/30/99	2.97	59.4	14.26	392.59	114.13	100.21	74.47
10	1/5/00	3.86	77.22	10.97	624.70	148.86	125.07	79.98
11	2/1/00	5.01	100	8.45	542.94	126.48	105.61	80.55
12	3/8/00	5.7	115	7.43	503.81	131.62	113.17	77.54
13	4/24/00	7	132	6.05	464.60	106.08	87.06	81.26
14	6/5/00	8	160	5.29	435.52	121.12	105.40	75.80
15	6/26/00	8.8	172	4.81	410.25	140.98	127.21	68.99
16	7/24/00	7.2	136.8	5.88	439.48	160.95	146.29	66.71
17	9/14/00							

Note: Without taking into account the system acclimation time which depends on the characteristics of the feed stream and the microbes

Figure 1. TOC Conversion Versus Hydraulic Residence Time for the MOE Unit

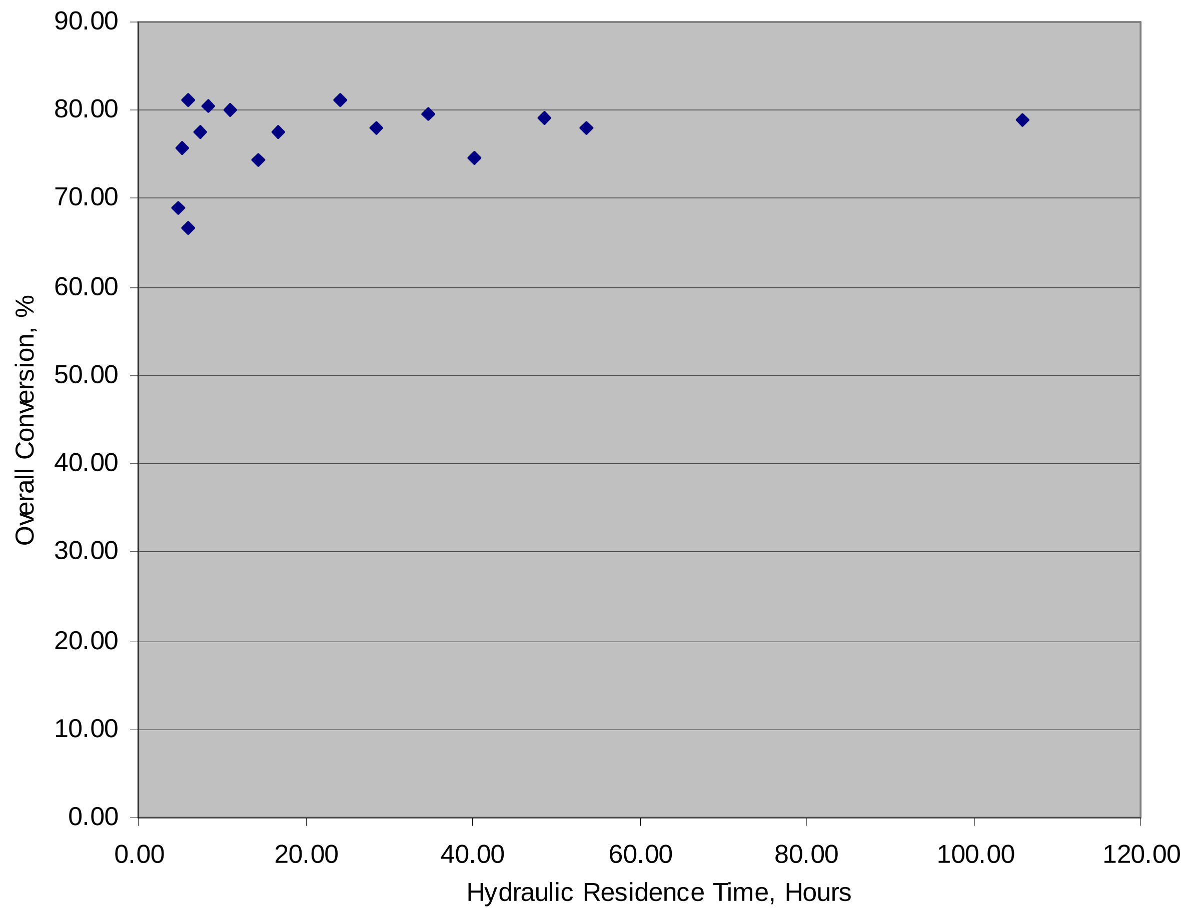


Table 2. Summary of Test Data for the MOE Unit (Single Pass Data)

Test point	Date	Qf, ml/min	Qr, ml/min	Vol. Flow, ml/min	Feed TOC, mg/l	Reactor Inlet TOC, mg/l	Reactor Effl. TOC, mg/l	RT, Hours	One-pass conv., %	Krate, (mg/l)^0.5/hr
1	6/22/99	0.4	7.9	8.3000	387.64	96.53	81.79	5.10	15.2702	0.153102079
2	7/19/99	0.79	15.7	16.4900	394.10	101.57	86.85	2.57	14.4920	0.295469759
3	8/10/99	0.87	17.5	18.3700	501.57	123.81	105.03	2.31	15.1687	0.381104502
4	9/7/99	1.05	20.9	21.9500	369.28	106.54	93.34	1.93	12.3900	0.342370603
5	9/26/99	1.22	24.4	25.6200	373.56	90.13	75.96	1.65	15.7238	0.470824107
6	10/5/99	1.48	29.6	31.0800	322.83	82.83	70.83	1.36	14.4869	0.502731179
7	10/11/99	1.75	41.9	43.6500	463.60	102.81	87.74	0.97	14.6566	0.796198879
8	11/12/99	2.53	51	53.5300	443.23	116.02	99.79	0.79	13.9912	0.988297463
9	11/30/99	2.97	59.4	62.3700	392.59	114.13	100.21	0.68	12.1986	0.990837909
10	1/5/00	3.86	77.22	81.0800	624.70	148.86	125.07	0.52	15.9788	1.947396754
11	2/1/00	5.01	100	105.0100	542.94	126.48	105.61	0.40	16.4972	2.403788879
12	3/8/00	5.7	115	120.7000	503.81	131.62	113.17	0.35	14.0161	2.377908057
13	4/24/00	7	132	139.0000	464.60	106.08	87.06	0.30	17.9232	3.178871712
14	6/5/00	8	160	168.0000	435.52	121.12	105.40	0.25	12.9790	2.931614762
15	6/26/00	8.8	172	180.8000	410.25	140.98	127.21	0.23	9.7716	2.540312576
16	7/24/00	7.2	136.8	144.0000	439.48	160.95	146.29	0.29	9.1083	2.011425366
17	9/14/00									

Note: Without taking into account the system acclimation time which depends on the characteristics of the feed stream and the microbes.

Figure 2. Single-Pass TOC Conversion Versus Residence Time for the MOE Unit

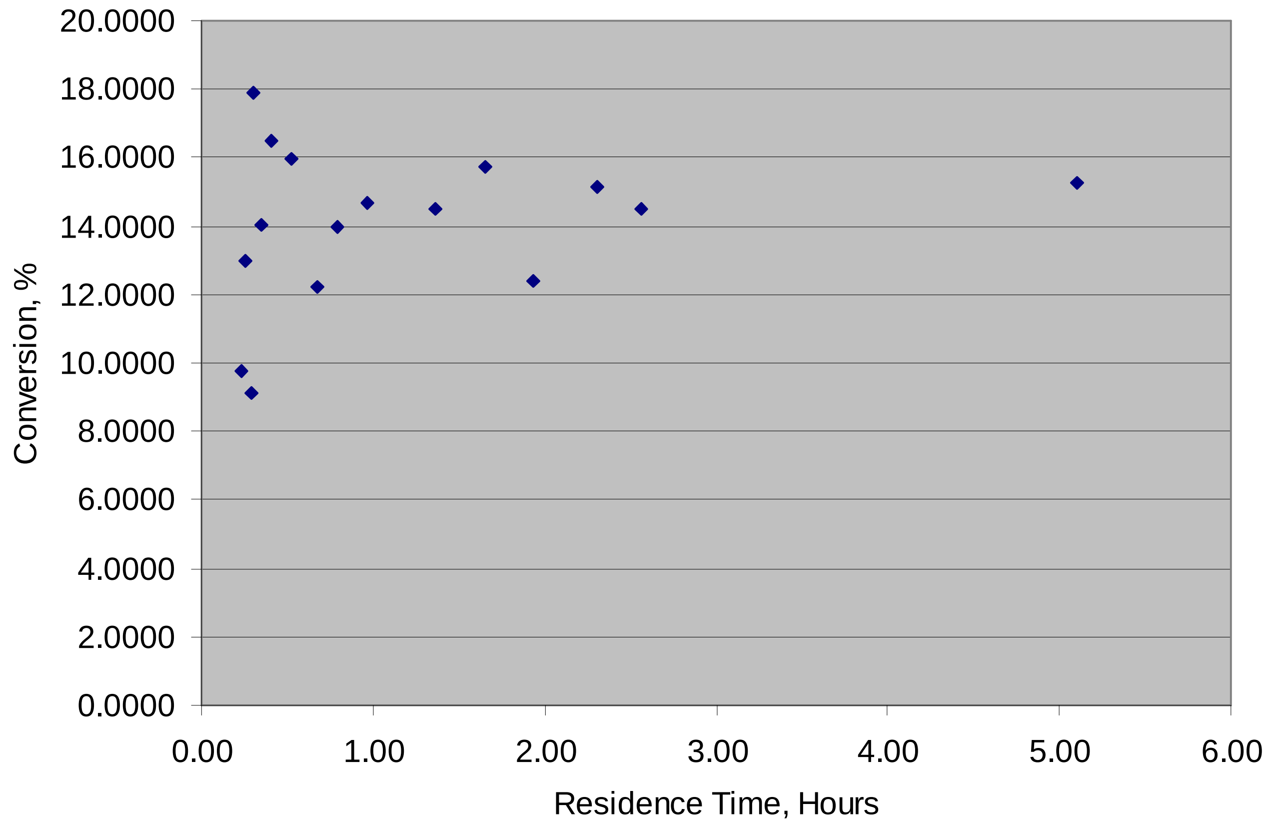
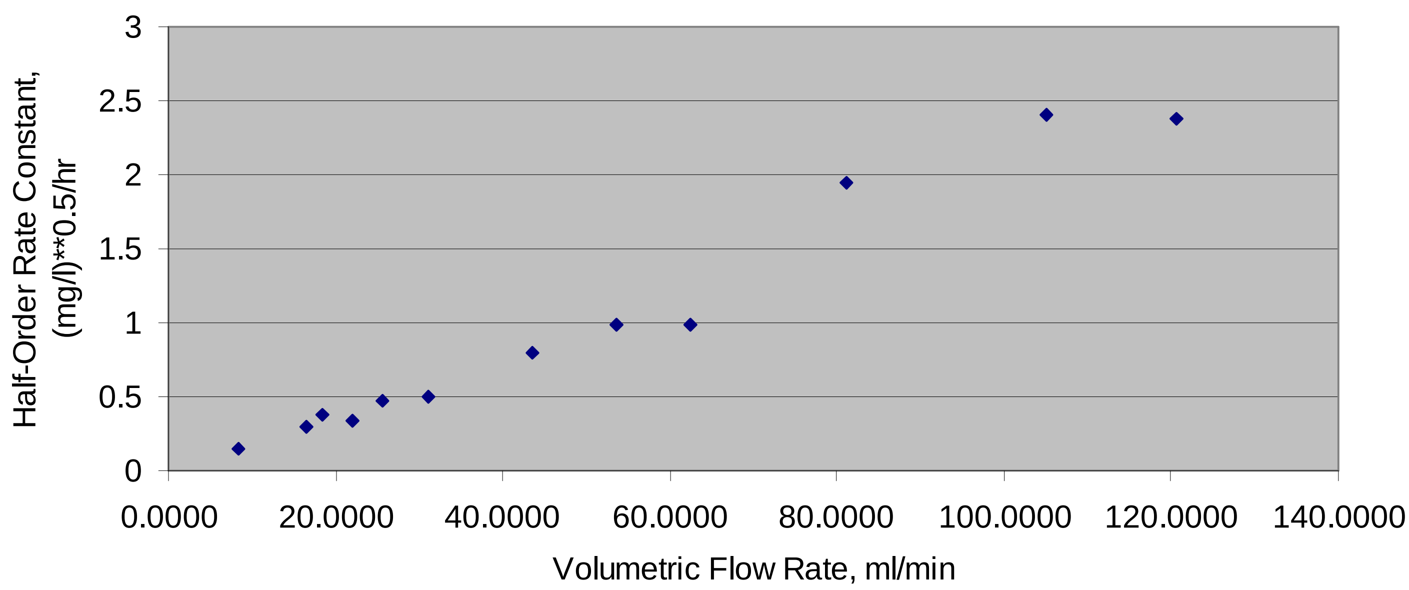


Figure 3. Reaction Rate Coefficient Versus Volumetric Flow



2. NITRIFICATION PROCESS

Literature search and data review

Literature search has been conducted to obtain experimental data similar to the operating conditions of JSC's Nitrification process for the development of the reaction kinetics.

The search indicates that none of the biofilm reactors in the public domain have the same configuration as JSC's tubular nitrification reactor, which is designed for zero-gravity application.

The nitrification data from the public domain show that nitrification reaction can follow the Monod kinetics or the Michaelis-Menten equation (Ref. 1). Some reports suggest that the nitrification kinetics can follow the zero-order kinetics or the first-order kinetics of a certain rate-limiting substrate, such as the ammonium concentration, oxygen concentration, organic matter concentration, etc. (Ref. 15-26). Further literature will be researched and reviewed to confirm on the nitrification kinetics.

Data Analysis of the SHEMP Unit's Nitrification Process

In order to upgrade the Nitrification module of the existing WRS ASPEN Plus model, test data from the SHEMP experimental unit were collected from Jayesh Gandhi/GB Tech.

Data reduction and correlation were conducted and the results are shown in the following.

Table 3 shows a summary of the SHEMP data. Figure 4 shows the relationship between the ammonium conversion and HRT for the SHEMP unit. More data collection and reviews are recommended before a more convincing conclusion can be drawn.

CONCLUSIONS AND RECOMMENDATIONS

Analysis tasks completed for the WRS Integration Testing are listed below:

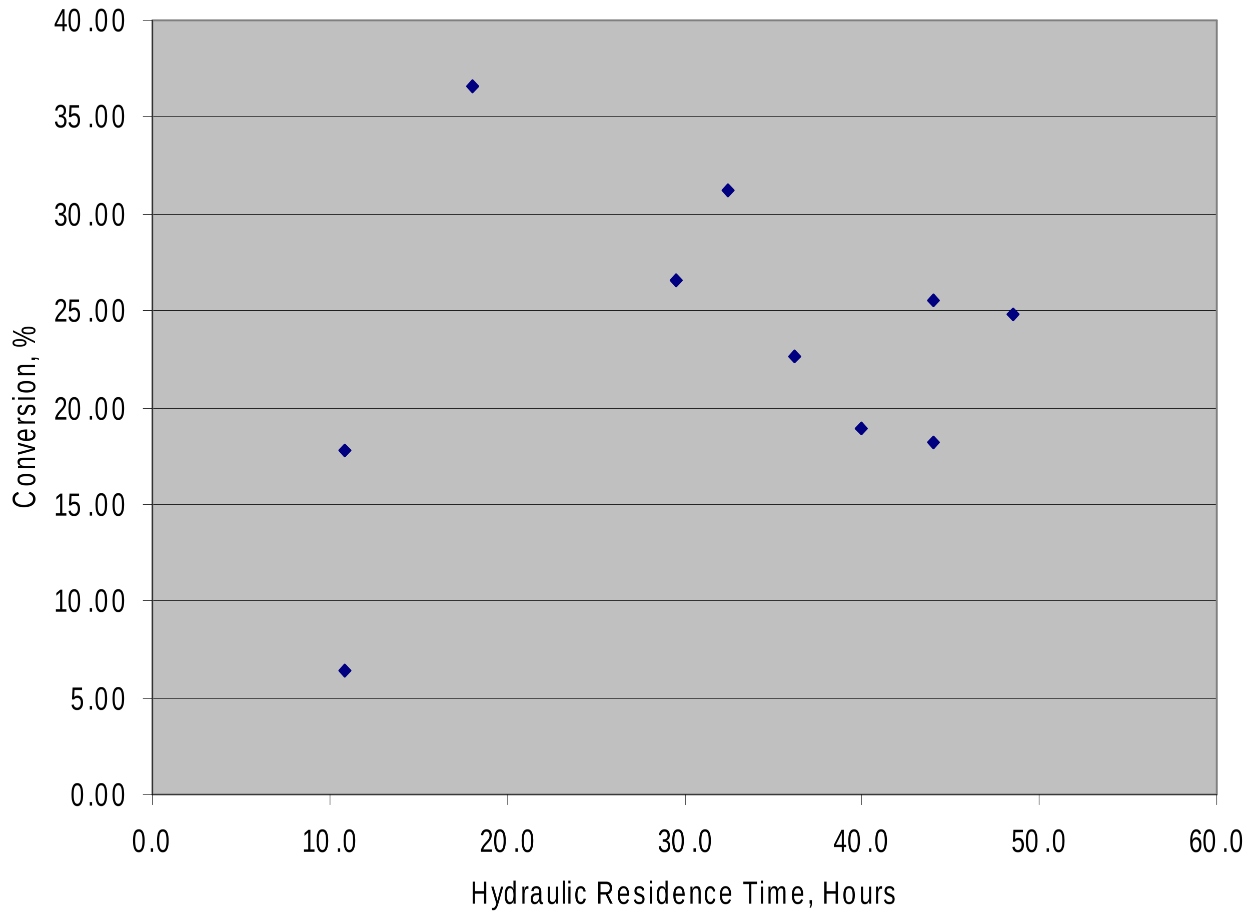
1. Implemented the Monod Kinetics to the TOC Removal Module of the WRS ASPEN Plus Model.
2. Implemented the half-order kinetics in a Fortran Block for the TOC Removal module.
3. Data analysis of the MOE experimental data collected between 6/22/99 and 4/23/2000 shows that the TOC conversion is independent of the HRT/RT in that time frame.
4. Review of published data suggests that the reaction kinetics of the TOC conversion can be zero or half-order for biofilm reactors. The reaction kinetics is dependent on the TOC concentration in the system and the degree of penetration of the substrate through the biofilm.
5. Data collected from the MOE TOC converter after 4/23/2000 enables the estimation of the minimum HRT or optimum HRT.
6. Numerous articles related to the nitrification process have been collected from the public domain and reviewed.
7. Collected SHEMP Nitrification data from JSC and correlated the experimental data.

Table 3. Summary of Test Data for the SHEMP Unit's Nitrification Process

Date	Flowrate, ml/min	Tube ID, inch	Tube Length, feet	Reactor Vol., ml	HRT, hours	Feed NH4 conc., ppm	Effluent NH4 conc., ppm	Conversion, %
6-Mar-00	0.79	0.125	1000	2300.98	48.5	250	188	24.83
21-Mar-00	0.87	0.125	1000	2300.98	44.1	143	117	18.16
5-Apr-00	0.87	0.125	1000	2300.98	44.1	128	95	25.51
10-Apr-00	0.96	0.125	1000	2300.98	39.9	296	240	18.91
22-May-00	1.06	0.125	1000	2300.98	36.2	163	126	22.67
5-Jun-00	1.18	0.125	1000	2300.98	32.5	121	83	31.17
26-Jun-00	1.3	0.125	1000	2300.98	29.5	181	133	26.52
25-Jul-00	1.06	0.125	500	1150.49	18.1	96	61	36.59
28-Jul-00	1.06	0.125	300	690.29	10.9	474	444	6.37
11-Aug-00	1.06	0.125	300	690.29	10.9	161	133	17.77
15-Sep-00								

Note: Without taking into account the system acclimation time (at start-up) which depends on the characteristics of the feed stream and the microbes.

Figure 4. Conversion versus Residence Time (SHEMP Nitrification Unit)



With the current experimental data collected, it is difficult to develop an accurate reaction kinetics model for the TOC removal process. We would recommend the WRS team to perform the following:

1. Perform additional experiments to collect a set of data specifically for the kinetics development. This needs to be done by running a set of experiments in parallel and each one in batch mode. The main focus is to quantify all the factors affecting the reaction rates, terminate the operation at different residence time, and analyze the TOC conversion for each experiment at the end of each termination.

2. Repeat the HRTs at 6.05, 8.45 and 24.2 hours for the TOC reactor to confirm the repeatability of the optimum data points.

3. Explore the nitrification's bioreactor technology, such as using the hollow fiber membrane, etc. Validate and confirm their performance in nitrification.

4. Run more lab scale tests on the nitrification bioreactors under different conditions and locate the optimum parameters, e.g. nutrient concentration, pH control, etc. prior to the scale-up of the process.

REFERENCES

1. Halling-Sorensen, B., and S.E. Jorgensen, "The Removal of Nitrogen Compounds from Wastewater," Elsevier Science Publishers B.V., 1993.

2. Harremoes, P., "Biofilm Kinetics," Water Pollution Microbiology, Volume II, pp. 71-109, 1978.

3. Mendonca, M. M. de, el al, "Short and Long-Term Responses to Changes in Hydraulic Loading in a Fixed Denitrifying Biofilm," Water Science Technology, Vol. 26, No. 3-4, pp.535-544, 1992.

4. Mishima, K., et al, "Characterization of Nitrification and Denitrification of the Media – Anaerobic-Anoxic- Oxic Process," Water Science Technology, Vol. 34, No 1-2, pp.137-143, Elsevier Science Ltd., 1996.

5. Riemer, M., et al, "Multi-component Diffusion in Denitrifying Biofilms," Prog. Water Technology, Vol. 10, No. 5-6, pp.149-165, 1978.

6. Cook, Ne. E., et al, "Denitrification of Potable Water in Packed Tower Biofilm," National Conference on Environment Engineering, pp. 175-182, 1990.

7. Aesoy, A., et al, "Denitrification in a Packed Bed Biofilm Reactor (Biofor) – Experiments with Different Carbon Sources," Water Research, Vol. 32, pp.1463-1470, 1998.

8. Takamizawa, K., et al, “Promotion of Nitrification and Denitrification by Recirculation of Effluent and Biofilm Process,” Environmental Technology, Vol. 14, pp. 981-987, 1993.

9. La Motta, E. J., “External Mass Transfer in a Biological Film Reactor,” Biotechnology and Bioengineering, John Wiley and Sons, Inc., pp. 1359-1370, 1976.

10. Aesoy, A., et al, “A Comparison of Biofilm Growth and Water Quality Changes in Sewers with Anoxic and Anaerobic (Septic) Conditions,” Water Science Technology, Vol. 36, No. 1, pp. 303-310, 1997.

11. Harremoes, P., “Half-Order Reactions in Biofilm and Filter Kinetics,” Vatten, pp. 122-143, 1977.

12. Harremoes, P., ”The Significance of Pore Diffusion to Filter Denitrification,” Water Pollution Control Federation, Vol. 48, pp. 377-388, 1976.

13. Ryhiner, G. S., et al, “Biofilm Reactors Configuration for Advanced Nutrient Removal,” Water Science and Technology, Vol. 20, pp. 111-117, 1993.

14. Wang, Z., “Application of Biofilm Kinetics to the Sulfur Lime Packed Bed Reactor for Autotrophic Denitrification of Groundwater,” Water Science Technology, Vol. 37, No. 9, pp. 97-104, 1998.

15. Anthonisen, A. C., et al, ”Inhibition of Nitrification by Ammonia and Nitrous Acid,” Journal WPCF, Vol. 48, No. 5, pp. 835-852, May 1976.

16. Atkinson, B., et al, “Overall Rate of Substrate Uptake (Reaction) by Microbial Films. Part I- A Biological Rate Equation,” Trans. Instn Chem. Engineers, Vol. 52, pp. 248-259, 1974.

17. Atkinson, B., et al, “Overall Rate of Substrate Uptake (Reaction) by Microbial Films. Part II – Effect of Concentration and Thickness with Mixed Microbial Films,” Trans. Instn Chem. Engineers, Vol. 52, pp. 260-268, 1974.

18. Aesoy, A., et al, “Upgrading Wastewater Treatment Plants by the Use of Biofilm Carriers, Oxygen Addition and Pre-Treatment in the Sewer Network,” Water Science Technology, Vol. 37, No. 9, pp. 159-166, 1998.

19. Andreadakis, A. D., “A Comparative Study of the Air and Oxygen Activated Sludge Systems,” Environmental Technology Letters, Vol. 8, pp. 209-220, 1987.

20. Yun, Y., et al, “Reclamation of Wastewater from a Steel-Making Plant Using an Airlift Submerged Biofilm Reactor,” J. of Chemical Technology and BioTechnology, Vol. 73, pp.162-168, 1998.

21. Zhu, S., et al, “An Experimental Study on Nitrification Biofilm Performance Using a Series Reactor System,” Aquacultural Engineering 20, pp. 245-259, 1999.

22. Memoud, P., et al, ”Simultaneous Nitrification and Denitrification Using Siporax Packing,” Water Science Technology, Vol. 40, No. 4-5, pp. 153-160, 1999.

23. Brindle, K., et al, ”Nitrification and Oxygen Utilization in a Membrane Aeration Bioreactor,” Journal of Membrane Science 144, pp.197-209, 1998.

24. De Beer, D., et al, “ Micro-Environments and Mass Transfer Phenomena in Biofilms Studied with Microsensors,” Water Science Technology, Vol. 39, No. 7, pp. 173-178, 1999.

25. Helmer, C., et al, “Nitrogen Loss in a Nitrifying Biofilm System,” Water Science Technology, Vol. 39, No. 7, pp. 13-21, 1999.

26. Lazarova, V., et al, “Influence of Operating Conditions on Population Dynamics in Nitrifying Biofilms,” Water Science Technology, Vol. 39, No. 7, pp. 5-11, 1999.